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Ordering of TiO_2 nanoparticles to mesoporous structures using block copolymers

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Introduction

Mesoporous, crystalline metal oxides are rapidly gaining importance for applications in sensors, (photo)catalysis and energy generation/storage. For most applications, the ideal material should be **crystalline** as well as **porous**, enhancing surface related phenomena. The commonly used synthetic procedures involve the creation of an amorphous network from solgel precursors templated by organic surfactants. This requires crystallization at elevated temperatures, which often results in a collapse of the mesostructure.

Two approaches will be investigated to tackle the trade-off between crystallinity and increased surface. The first encompasses the application **thermally stable block copolymers** to be used as pore formers suppressing shrinkage and collapse of the mesoporous structure during processing at elevated temperatures necessary to induce crystallinity. The second strategy consists of the **ordering of previously synthesized nanocrystals to porous structures** by using micelle forming block copolymers as ligands.

Sol-gel approach

A **surfactant** is mixed with a **Ti^{4+}- precursor** that hydrolyses and condenses around the supramolecular structure formed by the surfactant. In a next step the surfactant is removed by a **thermal procedure** which also **crystallizes the titania** (+ 400 °C). If the surfactant is degraded before the crystallization, the pores will collapse. Specific surfaces > 250 m^2/g are only reported for largely amorphous materials processed at reduced temperatures.(1)

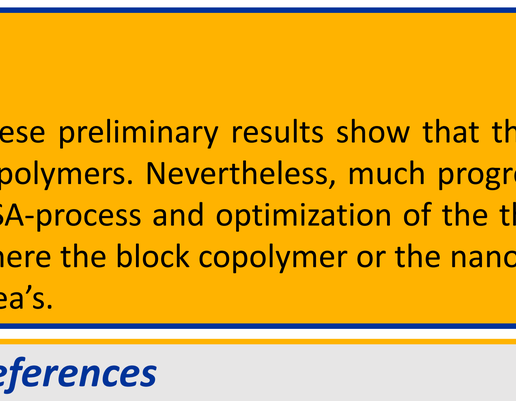


Figure 2: Formation of mesoporous TiO_2 using the sol-gel soft-templating synthesis route. The Ti-precursor hydrolyses and condenses around a supramolecular structure formed by a surfactant. This surfactant is removed by a thermal treatment.

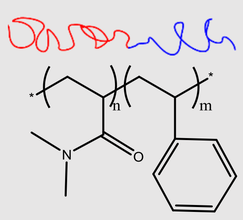
Block copolymers

Requirements polymer:

- Improved interaction with TiO_2(-nanocrystals)
- Synthesizable in a controlled manner: low dispersity
- Micellization in the TiO_2 nanocrystal suspensions

PDMA-b-PS (Poly(dimethylacrylamide)-block-polystyrene):

- Via Reversible Addition Fragmentation chainTransfer (RAFT)
- Variation of PDMA/PS ratio to obtain optimal supramolecular structure formation (hexagonal pores)

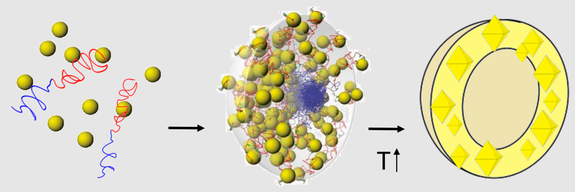


Polymer	PDMA (g/mol)	PS (g/mol)	PDI
PDMA-PS_{4k}	5000	4000	1.2
PDMA-PS_{5k}	5000	5000	1.26
PDMA-$PS_{7,5k}$	5000	7500	1.16
PDMA-PS_{9k}	5000	9000	1.18

Figure 1: Left: structure formula of PDMA-b-PS, right: table of the molecular weights and distperisity's of the different synthesized block copolymers

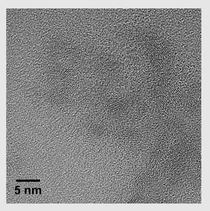
Nanocrystal Soft-templating approach

Nanocrystals are ordered into a porous structure with **suitable surfactant molecules**. This will lead to an important reduction of the processing temperatures: a **mild temperature treatment** is sufficient **to connect the particles** and remove the template.



Ultrasmall spherical nanoparticles are used:

- Microwave synthesis with tert-BuOH, toluene and $TiCl_4$ (2)
- Suspendable in EtOH



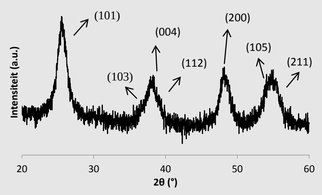
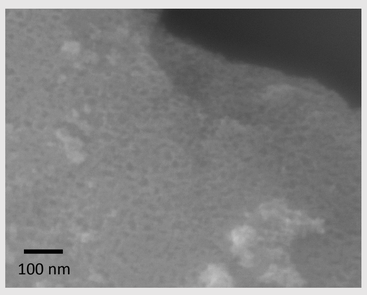


Figure 3: Left: a TEM- image, right: a XRD-pattern of the ultrasmall spherical nanoparticles. Nanocrystals of 4 nm are obtained.

Porous and crystalline powders

Synthesis procedure:

- PDMA-b-PS is dissolved in THF and EtOH is added to induce supramolecular aggregate formation (THF/EtOH : 1/3)
  - For sol-gel: HCl and Ti-isopropoxide are added
  - For NC-route: NC are suspended in EtOH
- Evaporation Induced Self-Assembly at 60°C
- Thermal treatment: 2h at 450 °C, 2°C/min



Sol-gel approach: BET surface area (m^2/g)	Polymer	Nanocrystal approach: BET surface area (m^2/g)
241	PDMA-PS_{4k}	86
211	PDMA-PS_{5k}	/
192	PDMA-$PS_{7,5k}$	97
215	PDMA-PS_{9k}	88

Figure 4: Respectively a SEM image of the porous TiO_2 powder obtained by the PDMA-PS_{4k} polymer and a table of the BET-surface area's obtained with the different block copolymers and synthesis routes.

Conclusions

These preliminary results show that the current state of the art for mesoporous and crystalline TiO_2 (250 m^2/g) can be reached using the self-synthesized PDMA-b-PS block copolymers. Nevertheless, much progress can still be made by varying the concentrations of polymers and Ti-precursor, adapting the temperature and moisture levels of the EISA-process and optimization of the thermal treatment. Worse results were obtained for the nanocrystal route but only a few tests with unstable solutions were performed, where the block copolymer or the nanocrystals precipitated. Furthermore it will be investigated if a lower thermal treatment temperature (f.e. 375 °C) will lead to higher surface area's.

References

1. Meynen V and Cool P, Microporous and Mesoporous Materials, 2009, **125**, 170.
2. Szeifert JM and Feckl JM, Journal of the American Chemical Society, 2010, **132**, 12605

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